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# Quantifying the effects of neglecting many-body interactions in coarse-grained models of complex fluids

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We describe a general simulation scheme for assessing the thermodynamic consequences of neglecting many-body effects in coarse-grained models of complex fluids. The method exploits the fact that the asymptote of a simple-to-measure structural function provides direct estimates of virial coefficients. Comparing the virial coefficients of an atomistically detailed system with those of a coarse-grained version described by pair potentials, permits the role of many-body effects to be quantified. The approach is applied to two models: (i) a size-asymmetrical colloid-polymer mixture, and (ii) a solution of star polymers. In the latter case, coarse-graining to an effective fluid described by pair potentials is found to neglect important aspects of the true behaviour.

Many-body forces occur when the net interaction between two particles is not simply pairwise additive, but depends on the presence of other particles. They appear in a wide range of physical systems including dense phases of noble gases [1], molecular systems [2], nuclear matter [3], superconductors [4] and complex fluids such as polymers [5], lipid membranes [6, 7] and colloidal dispersions [8–11]. In seeking to make theoretical and computational progress with such systems one often attempts to simplify matters by “coarse-graining” ie. integrating over the degrees of freedom on small length or times scales. This leads to a description of the system in term of an effective Hamiltonian describing the interactions among the remaining degrees of freedom. These interactions are inherently many-body in character, even if the original system involves only pairwise interactions.

To appreciate how many-body interactions arise in coarse-grained (CG) representations of complex fluids, consider the case of colloids dispersed in a sea of much smaller polymers. This system is commonly modelled as a highly size-asymmetrical mixture of spheres as shown in the simulation snapshot of Fig. 1(a). However, since dealing with components of disparate sizes is theoretically and computationally problematic, one typically seeks to integrate out the polymer degrees of freedom to yield an effective one-component model. But the colloidal interactions arise from the modulation of the polymer density distribution by *all* the colloids, and consequently, the effective one-component description is many-body in form. A second example is shown in Fig. 1(b) which depicts three star polymers in solution. A common CG model replaces each star by a single effective particle. However, the net interaction between two polymers depends on the proximity of a third, and hence the effective Hamiltonian has a many-body character [12].

Computer simulation is a powerful route for designing CG models for complex fluids, which is currently receiving considerable attention. Indeed, in principle it can be used to determine a many-body potential for the CG co-ordinates which is consistent with the underlying atomistic model [13, 14]. But implementing such approaches

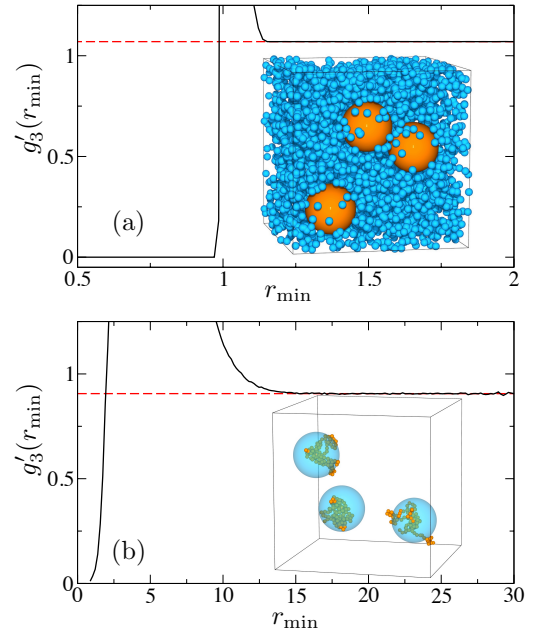


FIG. 1. (Color online). (a) Snapshot of a highly size-asymmetrical mixture of spheres. The effective one-component model is realized by integrating out the small sphere degrees of freedom. (b) A snapshot of three star polymers. The big spheres represent a coarse grained model in which each polymer is replaced by a single effective particle. In both (a) and (b) simulation measurements are also shown for the structural quantity  $g'_3(r_{\min})$  discussed in the text, whose asymptote (dashed) yields information on the third virial coefficient.

is far from trivial and it is still the norm that CG descriptions neglect some or all many-body effects [15–18]. Thus for polymers one might replace each chain by a set of one or more ‘blobs’ which interact via a pair potential such as the potential of mean force [19]. Similarly for a colloid-polymer mixture one typically describes the colloidal interactions via the depletion pair potential [20]. In view of this, it is patently important to be able to assess the likely implications of the pair potential approximation for the thermodynamics of the CG system. To date,

though, there has been little in the way of systematic methods for doing so.

In this Letter we introduce a widely applicable tool for comparing some basic thermodynamic properties of an atomistically detailed system with those of its CG representation. Our approach is based on calculations of the virial coefficients  $B_n$ . These are pertinent because they provide a systematic expansion of the properties of a system in terms of many-body interactions:  $B_2$  depends only on pair interactions, while  $B_3$  depends on two- and three-body interactions, etc. Comparison of virial coefficients for the atomistically detailed and CG models provide a measure of the extent to which the thermodynamics of the models agree.

Previously there has been no method capable of directly determining virial coefficients for complex fluids. The novel feature of our approach is that it is based on exploiting *finite-size effects*. Consider a simulation box of volume  $V$  containing  $N$  interacting molecules in thermal equilibrium at inverse temperature  $\beta = (k_B T)^{-1}$ . For each of the  $N$  molecules we tag an arbitrary atomic site and label its position vector  $\mathbf{r}_i$ , with  $i = 1 \dots N$ . The position vectors of the remaining  $m$  atoms in each molecule we write as  $\mathbf{r}_{i,j} = \mathbf{r}_i + \mathbf{u}_{i,j}$ ,  $j = 1 \dots m$ , with  $\mathbf{u}_{i,j}$  the displacement of atom  $j$  on molecule  $i$  from the tagged atom  $\mathbf{r}_i$ . Accordingly a molecular configuration can be specified via a list of the  $N$  tagged and the  $M = Nm$  non-tagged coordinates,  $\mathbf{r}^N, \mathbf{u}^M$ . The corresponding Boltzmann probability is

$$P_N(\mathbf{r}^N, \mathbf{u}^M) = \frac{e^{-\beta U(\mathbf{r}^N, \mathbf{u}^M)}}{Z_N}, \quad (1)$$

where  $U(\mathbf{r}^N, \mathbf{u}^M)$  is the full interaction potential containing both intra and intermolecular terms and

$$Z_N = \int e^{-\beta U(\mathbf{r}^N, \mathbf{u}^M)} d\mathbf{r}^N d\mathbf{u}^M \quad (2)$$

is the  $N$ -molecule configurational integral.

Now define

$$\tilde{g}_N(\mathbf{r}^N, \mathbf{u}^M) \equiv \frac{P_N(\mathbf{r}^N, \mathbf{u}^M)}{P_N^{\text{ig}}(\mathbf{r}^N)} = V^N \frac{e^{-\beta U(\mathbf{r}^N, \mathbf{u}^M)}}{Z_N}, \quad (3)$$

where  $P_N^{\text{ig}}(\mathbf{r}^N) = V^{-N}$  is the probability of finding (within the same volume) a set of  $N$  structureless ideal gas particles in the same configuration as the tagged sites. We shall focus on the low density limit of  $\tilde{g}_N(\mathbf{r}^N, \mathbf{u}^N)$ , corresponding to  $|\mathbf{r}_k - \mathbf{r}_l| \rightarrow \infty$ ,  $\forall k, l$ . In this regime the molecules are non-interacting, so we can integrate out the internal molecular degrees of freedom (associated with the  $\mathbf{u}_{i,j}$ ) to obtain the asymptotic value

$$f_N(V) \equiv \lim_{|\mathbf{r}_k - \mathbf{r}_l| \rightarrow \infty} \tilde{g}_N(\mathbf{r}^N) = \frac{(\Omega V)^N}{Z_N} = \frac{Z_1^N}{Z_N}, \quad (4)$$

where  $\Omega$  is the integral over the internal degrees of freedom of a single molecule and  $Z_1$  is the corresponding configurational integral.

The quantity  $f_N(V) = Z_1^N/Z_N$  is central because it permits a direct calculation of molecular virial coefficients as will be shown below. A key feature is its dependence on the system volume. Specifically, although it has the limiting behaviour  $\lim_{V \rightarrow \infty} f_N(V) = 1$ , for finite system volume  $f_N(V)$  deviates from unity. However, on the face of it, determining  $f_N(V)$  by simulation via eq. 4 is not a feasible proposition since it entails populating a  $3N$ -dimensional histogram for  $P_N(\mathbf{r}^N)$  with sufficient statistics to yield precise probabilities. Fortunately, though, it turns out to be possible to determine  $f_N(V)$  using only one-dimensional histograms. To see this, consider the quantity

$$g'_N(r_{\min}) \equiv \frac{P_N(r_{\min})}{P_N^{\text{ig}}(r_{\min})}. \quad (5)$$

Here  $r_{\min}$  is, for some configuration, the smallest, ie. the *minimum* separation among the  $N$  tagged sites. In the course of a simulation, one can accumulate histograms for  $P_N(r_{\min})$  and  $P_N^{\text{ig}}(r_{\min})$  and thus form  $g'_N(r_{\min})$ . Clearly, though, the limit  $r_{\min} \rightarrow \infty$  is none other than the limit  $|\mathbf{r}_k - \mathbf{r}_l| \rightarrow \infty$ ,  $\forall k, l$ . Moreover, since in this limit the microstates of the tagged particles are visited with constant probability  $\Omega^N Z_N^{-1}$ , while those of the ideal gas are visited with probability  $V^{-N}$ , it follows that the limiting value of  $g'_N(r_{\min})$  is the same as that of  $\tilde{g}_N(\mathbf{r}^N)$ , i.e.

$$\lim_{r_{\min} \rightarrow \infty} g'_N(r_{\min}) = f_N(V). \quad (6)$$

Eq. 6 provides a straightforward computational prescription for determining  $f_N(V)$ , which in turn permits the calculation of the virial coefficients for the molecular system. Specifically, from the virial cluster expansion [21] one finds that for  $N = 2$  particles

$$B_2 = \frac{V}{2} \left( 1 - \frac{Z_2}{Z_1^2} \right) = \frac{V}{2} \left( 1 - \frac{1}{f_2(V)} \right). \quad (7)$$

Similarly for three particles one finds

$$\begin{aligned} B_3 &= \frac{V^2(Z_1^4 - 3Z_2Z_1^2 - Z_3Z_1 + 3Z_2^2)}{3Z_1^4} \\ &= 4B_2^2 - 2B_2V + V^2 \frac{(f_3(V) - 1)}{3f_3(V)}. \end{aligned} \quad (8)$$

More generally, knowledge of  $f_\gamma(V)$ ,  $\gamma = 2, \dots, n$  permits the calculation of the virial coefficient  $B_n$ .

Thus measurements (for a small number of molecules) of the asymptotic value of a simple-to-measure structural quantity,  $g'_N(r_{\min})$ , provide direct access to molecular virial coefficients. The utility of the approach is wide because it can be used in conjunction with any simulation method capable of producing equilibrium configurations, for example Molecular Dynamics (MD), Monte

Carlo (MC) or Langevin Dynamics. Furthermore it can deal with much more complex systems than is possible with an existing method [22].

In general one can estimate  $f$  visually, or from a fit. However, we have found that a particularly accurate measure results from the ratio of integrals

$$f_N(V) = \frac{\int_{r_l}^{r_u} P_N(r_{\min}) dr_{\min}}{\int_{r_l}^{r_u} P_N^{\text{ig}}(r_{\min}) dr_{\min}}, \quad (9)$$

where  $r_l$  is some value of  $r_{\min}$  for which  $g'(r_{\min})$  can be considered to have first reached its limiting value, and  $r_u$  is the largest value of  $r_{\min}$  for which data has been accumulated, which will typically be half the simulation box diagonal length. It should be emphasized that in practice eq. (9) is evaluated simply from a count of entries in the respective histograms for  $P_N(r_{\min})$  and  $P_N^{\text{ig}}(r_{\min})$ —no numerical quadrature is necessary.

$N$	$V$	$B_N$	$B_N^{\text{exact}}[23]$
2	$(2.5\sigma)^3$	$2.09441(6)\sigma^3$	$2.0943951\dots\sigma^3$
3	$(3.5\sigma)^3$	$2.7418(4)\sigma^6$	$2.7415567\dots\sigma^6$
4	$(3.5\sigma)^3$	$2.629(22)\sigma^9$	$2.6362180\dots\sigma^9$

TABLE I. Estimates of the first four virial coefficients of hard spheres, compared with exact values.

To test the method we have used it to estimate the first few virial coefficients of a single component system of hard spheres of diameter  $\sigma$ , finding excellent agreement with exact values (see Tab. I). Having validated the method on a simple system, we turn to a more challenging problem, namely that of quantifying the scale of many-body effects in CG models for colloid-polymer mixtures. In such systems the polymers mediate effective colloidal interactions [20]. A commonly studied model treats the colloids as big hard spheres of diameter  $\sigma_b$ , and the polymers as small hard spheres of diameter  $\sigma_s$ , so that the size ratio is  $q \equiv \sigma_s/\sigma_b$ . The effective Hamiltonian then provides a CG description of the colloidal interactions in which the polymer degrees of freedom have been integrated out. Quite generally it takes the form  $H^{\text{eff}} = H^0 + \Theta$  where  $H^0$  is the bare colloid-colloid interaction, while  $\Theta$  is a many-body contribution arising from the polymers, which can in turn be written as a sum over  $n$ -body terms  $\Theta = \sum_{n=1}^{\infty} \theta_n$  [24]. Common practice is to approximate this Hamiltonian in terms of a sum over pair interactions, i.e.  $H^{\text{eff}} \approx \sum_{i,j} [\phi(r_{ij}) + W(r_{ij})]$  where  $\phi(r_{ij})$  is the hard sphere interaction between a pair of colloids whose centers are separated by a distance  $r_{ij}$ , while  $W(r_{ij})$  is the depletion pair potential, whose form depends on the small particle volume fraction and model details such as the degree of additivity of the big-small interaction. Usually one assumes that the small particles occupy an open ensemble, so that  $W(r)$  is parameterized in terms of the reservoir volume fraction  $\eta_s^r$ .

Since the depletion pair potential plays a central role in theories and simulations of colloid-polymer mixtures, it is desirable to quantify the effects of neglecting higher order terms in  $H^{\text{eff}}$ , the most prominent of which is triplet interactions. Our strategy for doing so estimates the third virial coefficient  $B_3^{\text{eff}}$  for the full effective fluid and compares it with the corresponding value  $B_3^{\text{dep}}$  for three particles interacting via the depletion pair potential. This comparison directly probes the extent to which the interaction between a pair of big particles is influenced by the proximity of a third one.

To obtain estimates for  $B_3^{\text{eff}}$  we deploy the geometrical cluster algorithm (GCA) [25, 26]. This efficient rejection-free Monte Carlo scheme can generate equilibrium configurations at practically any value of  $q$ . We have used it to study systems of  $N = 2$  and  $N = 3$  big particles in a sea of small ones at various  $\eta_s^r$ . The procedure is as follows:

- (i) In a simulation of  $N = 2$  tagged big particles, measure the form of  $g_2'(r)$  at some prescribed  $\eta_s^r$ . This yields the value of  $B_2^{\text{eff}}(\eta_s^r)$  via eq. (7).
- (ii) Use the form of  $g_2'(r)$  obtained in (i) to estimate the depletion potential  $W(r|\eta_s^r)$  by employing the procedure detailed by Ashton *et al* [27].
- (iii) Next simulate  $N = 3$  tagged big particles at the same value of  $\eta_s^r$  and measure  $\tilde{g}_3(r_{\min})$ . Together with the estimate of  $B_2^{\text{eff}}(\eta_s^r)$  obtained in (i), this yields an estimate for  $B_3^{\text{eff}}(\eta_s^r)$  via eq. (8).
- (iv) Finally perform a simple MC simulation of three particles interacting via the depletion potential  $W(r|\eta_s^r)$  obtained in (ii). This yields the third virial coefficient  $B_3^{\text{dep}}(\eta_s^r)$  via eq. (8).

We have applied this procedure to study two models of colloid-polymer mixtures, namely the Asakura-Oosawa (AO) model and a system of additive hard spheres. The AO model describes colloidal hard-spheres in a solvent of ideal polymer that have a hard-particle interaction with the colloids [28, 29], c.f. Fig. 1(a). Owing to its extreme non-additivity, the exact form of the depletion potential is known analytically [29] which obviates the need to perform steps (i) and (ii) above. Furthermore many-body forces are known to vanish for size ratios  $q < 0.1547$  [30, 31], a fact that allows us to further test our methodology and its sensitivity.

Fig. 1(a) includes a sample plot of  $g_3'(r_{\min})$  obtained for the AO model using a box of size  $V = (3.5\sigma_l)^3$  at  $\eta_s^r = 0.2, q = 0.154$ . The data show the approach to the asymptote,  $f_3(V)$ . From plots such as this we have obtained estimates of  $B_3^{\text{eff}}$  and  $B_3^{\text{dep}}$  for size ratios  $q = 0.5, 0.25, 0.154$ , as shown in Fig. 2. One expects that triplet interactions, as quantified by the difference between  $B_3^{\text{eff}}(\eta_s^r)$  and  $B_3^{\text{dep}}(\eta_s^r)$ , should increase with  $\eta_s^r$  and this is indeed the case. We find that  $B_3^{\text{eff}} > B_3^{\text{dep}}$ ,

consistent with the fact that triplet interactions weaken the attraction between particles [32]. One further expects  $B_3^{\text{eff}} - B_3^{\text{dep}}$  to diminish with decreasing  $q$  and have vanished by  $q = 0.154$ , a feature which is confirmed to high precision by our data.

For additive hard spheres, the GCA is considerably less efficient than for the AO model being limited to  $\eta_s^r \lesssim 0.2$ . Although triplet interactions are always present in principle, our results (not shown) indicate that within this more limited range of  $\eta_s^r$ , they are negligibly small for  $q = 0.2$  and  $q = 0.1$ . This finding suggests that for applications at low to moderate  $\eta_s^r$  and small  $q$  it is safe to use depletion potentials for additive hard spheres.

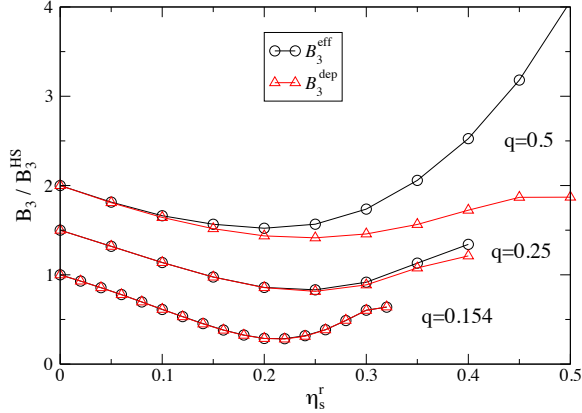


FIG. 2. Comparison of  $B_3^{\text{eff}}(\eta_s^r)$ , and  $B_3^{\text{dep}}(\eta_s^r)$  for the AO model with size ratios  $q = 0.5, 0.25, 0.154$ . Lines are guides to the eye and statistical uncertainties are smaller than the symbol sizes. To aid visibility, the curves for  $q = 0.25$  and  $q = 0.5$  have been shifted vertically by 0.5 and 1.0 respectively.

As a final illustration of the power and generality of our method, we have used it to quantify the role of triplet interactions in a model for star polymers in implicit solvent, c.f. Fig. 1(b). Each star comprises a core particle to which are attached a number (called the “functionality”) of linear polymer chains each comprising  $n$  monomers. Bonded monomers interact via a FENE spring, while non bonded monomers experience a Lennard-Jones (LJ) potential. Using MD we have studied various combination of functionality and chain length  $n$ . Our aim was to determine how these parameters affect the size of the triplet interactions. In order to effect this comparison in a fair manner, we tuned the temperature in each case such that  $B_2$  matches a prescribed value, thereby providing a “corresponding state”. The procedure for measuring the size of triplet interactions via virial coefficients is similar to that outlined for the colloid-polymer mixtures, except that the tagged particles are now taken to be the set of core atoms. The pair potential is the potential of mean force (pmf) which is obtained in a simulation of two stars. We then simulate three particles interacting via this potential to obtain  $B_3^{\text{pmf}}$ . This we compare with

$B_3^{\text{star}}$ , measured in a simulation of  $N = 3$  star polymers (a sample plot of  $g_3'(r_{\min})$  in a box of volume  $V = (40\sigma)^3$  is included in Fig. 1(b)).

The results are shown in Fig. 3 and reveal large discrepancies between  $B_3^{\text{pmf}}$  and  $B_3^{\text{star}}$ , which decrease in magnitude as both the functionality and the arm length increase. Clearly the disparity is such that one should expect a quite different equation of state (as well as other thermodynamic quantities) to arise from the coarse-grained system described by the pmf compared to the full model. We believe that the importance of many-body effects in this system arises from the ability of the polymers to substantially overlap, which occurs predominantly for lower functionality and smaller number of monomers per arm. When two polymers overlap, the resulting composite particle is locally much denser than for a single polymer. Accordingly a third polymer is much less likely to overlap with the first two due to short ranged monomeric repulsions. Clearly, however, this effect is completely neglected in the pair potential framework. This observation should be relevant to CG models for many other types of polymer-based soft particles, including cluster forming amphiphilic dendrimers [33].

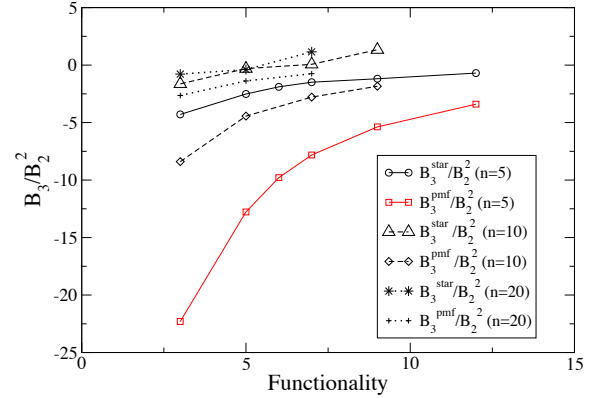


FIG. 3. Estimates of the dimensionless third virials  $B_3^{\text{pmf}}/B_2^2$  and  $B_3^{\text{star}}/B_2^2$  vs functionality for various chain lengths  $n$ . Volumes ranged from  $V = (20\sigma)^3$  to  $V = (40\sigma)^3$ , large enough to access the limiting behaviour of  $g_3'(r_{\min})$ . Bonded monomers interact via a FENE potential with parameters  $K = 30.0\epsilon/\sigma^2$ ,  $R_0 = 1.5\sigma$  [34]. The LJ potential was truncated and shifted at  $r = 2.5\sigma$ . In all cases  $T$  is chosen to yield  $B_2 = -3321\sigma^3$ . Errors are comparable with symbol sizes.

In summary, we have proposed a general method for calculating low-order virial coefficients of complex fluids via a simple-to-measure structural property. The method is the only direct approach (of which we are aware) for achieving this. We have highlighted its utility in quantifying the consequences of neglecting many-body effects in coarse-graining schemes. Beyond this it should prove useful as a means of testing new and existing molecular models by comparing the extent to which they reproduce experimentally determined virial coefficients.

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